LA-UR-15-23328

Title: Plutonium Oxidation A chronological Perspective 1941-2003

Author(s): Stakebake, Jerry L.
Allen, Thomas Howard

Intended for: This presentation will be used as a reference in a current publication (LA-UR-15-21079). All of the references in that publication should be available for review.

Issued: 2015-05-01

PLUTONIUM OXIDATION

A CHRONOLOGICAL PERSPECTIVE 1941-2003

Jerry L. Stakebake

Thomas Allen (1)

May 22, 2003

(1) Mr. J. L. Stakebake is the **sole contributor** to the technical content of this presentation. Mr. Allen is added **only** as the submitter and administrative contact needed for publication.

OBJECTIVE

- Describe the evolution of the Pu oxidation studies.
- Present the current understanding of plutonium oxidation.
- Describe experimental methods.
- Discuss “real world” applications of oxidation data.
- Present storage case studies.
- Where do we go from here?

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

SCOPE

- Oxidation kinetic studies
  - Experimental techniques
  - Environmental effects
    - Oxygen
    - Moisture
    - Nitrogen
    - Hydrogen
    - Water and Sea Water
  - Material (alloy) effects
- Pyrophoric characteristics
- Storage behavior

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

EXPERIMENTAL METHODS

- Balance weight gain measurements of coupons
- TGA – Semi-micro and microbalance measurements
- Ellipsometric film thickness measurements
- X-ray diffraction
  - Product identification
  - Oxide film thickness
- XPS – X-Ray Photoelectron Spectroscopy
- Electron Microprobe, SEM

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

THE EARLY YEARS
Prior to 1960

- General Observations
  - Pu is reactive – subject to corrosion
  - Air oxidation enhanced by moisture
  - Relatively inert in dry air
  - Extensive corrosion in inert gases
  - Effect of alloying is dependent on the alloy
  - Unpredictable pyrophoric behavior of Pu
  - Pyrophoricity of corrosion products

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

THE EARLY YEARS
Prior to 1960

- **<u>QUESTION FOR THE DAY</u>**

When was the first oxidation experiment conducted?

Where?

By whom?

What were the results?

THE EARLY YEARS
1941 - 1960

- The First Experimental Oxidation Experiment
  - Berkeley, February, 1941
  - Seaborg, Wahl, Kennedy, and McMillan
  - Minute quantity of new synthetic element (94) was oxidized
  - Experiment was key step in proof of existence of Pu

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

THE EARLY YEARS
1941 – 1960

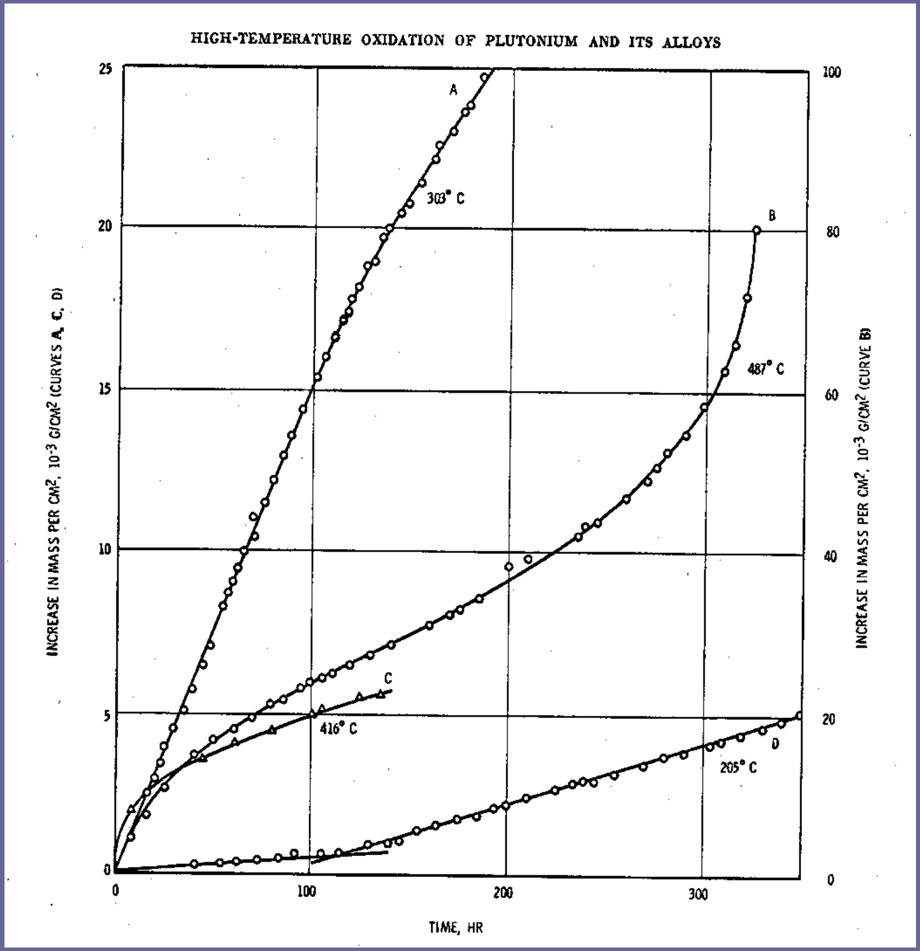
- Experimental Studies
  - Kolodney – 1945 – small coupons showed effects of temperature and moisture.
  - Dempsey and Kay – 1957; Preliminary results
    - Temperature 40 – 487°C
    - 0% and 100% Relative Humidity
  - Findings reported by Dempsey and Kay and reinforced by others later:
    - Interference colors for oxide films
    - Kinetic anomalies near phase Pu boundaries
    - Pyrophoricity and Ignition Temperatures
- Numerous experiments initiated

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

THE EARLY YEARS
1941 – 1960

- Oxidation of Pu in air
- 205°,303°,416°, and 487°C
- Introduction of kinetic anomalies

- Dempsey & Kay 1958

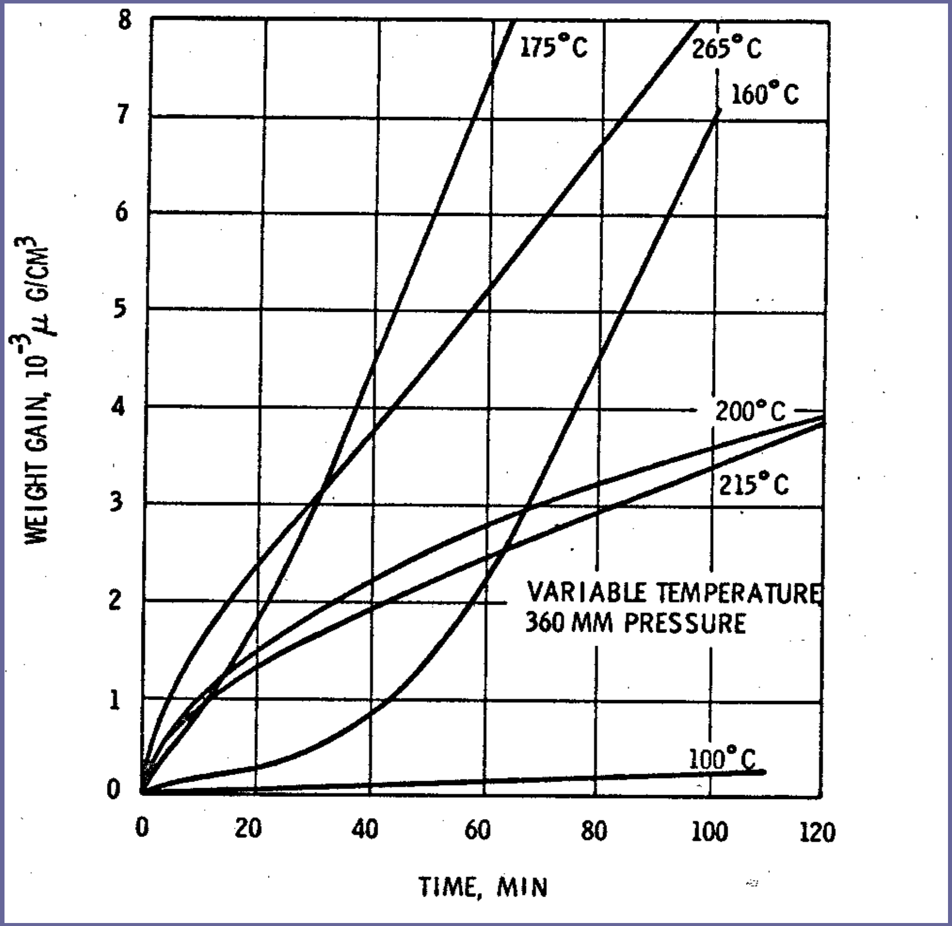


Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

THE PROLIFIC YEARS
1960 - 1985

- Air oxidation of Pu
- Anomalous kinetic behavior at low temperatures
- Caused by Pu metal phase change ????????

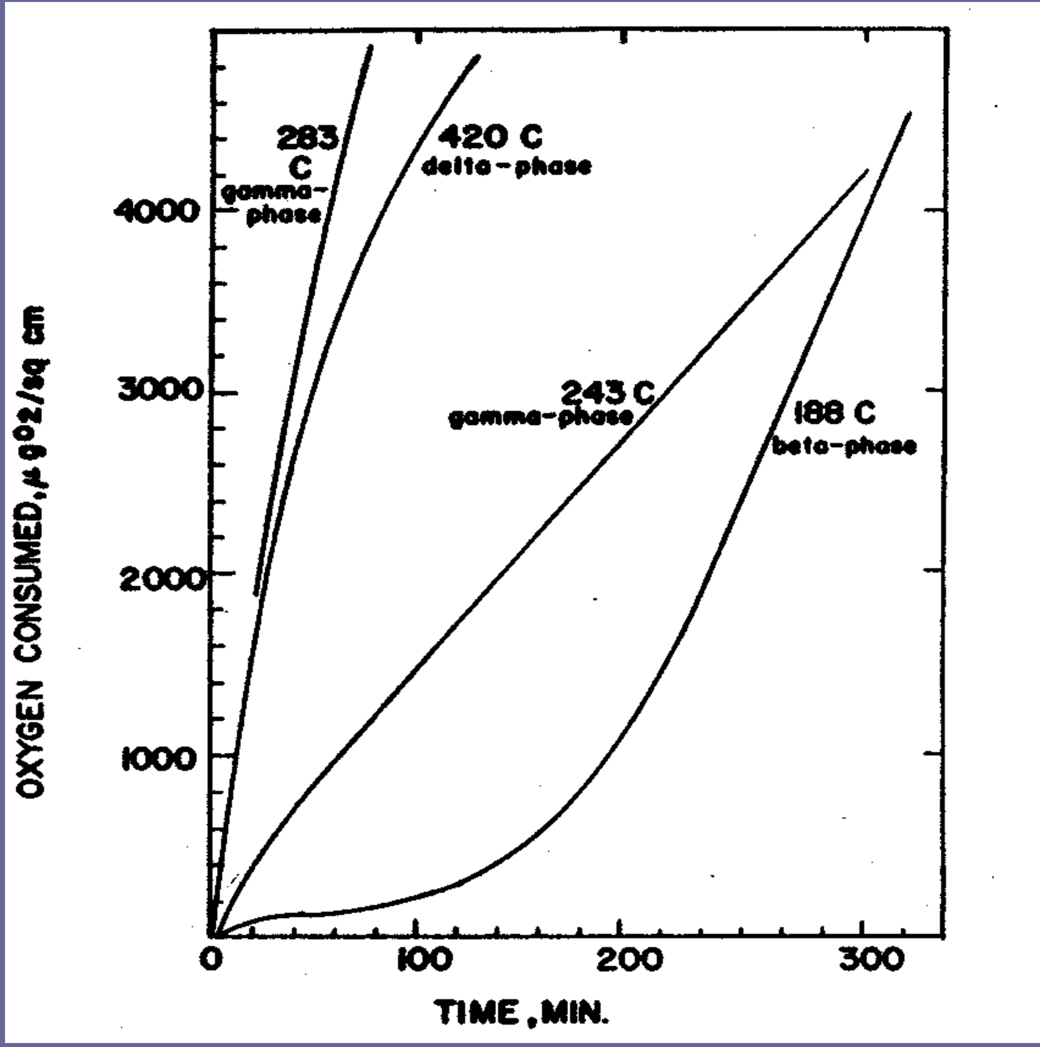
- Thompson - 1963



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Oxidation of Unalloyed Pu

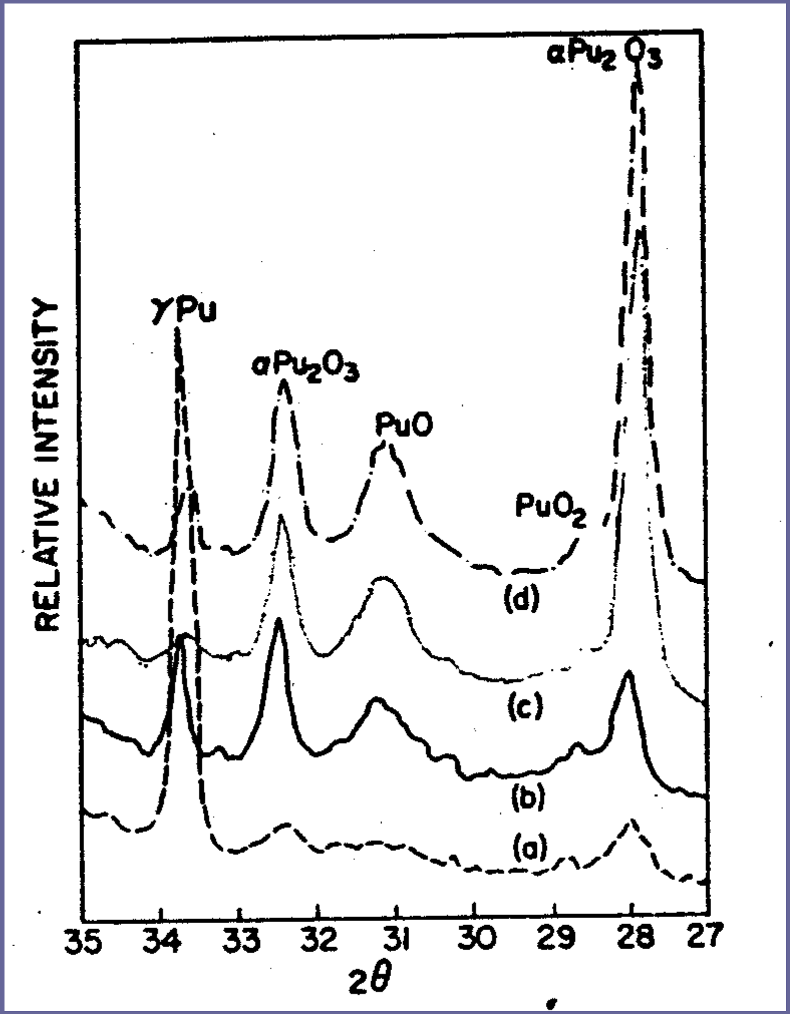
- Air – 200 ppm H_2O
- 3 Stage Kinetics
  - Parabolic
  - Linear
  - Transition/Linear
- Temperature Effect
  - Kinetic anomaly at 400°C
  - High self-heating at T>408°C
- [Schnizlein and Fischer]



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

X-Ray Diffraction of Pu Oxides

- Oxidation of Pu in O_2 at 305°C (Rate Maximum)
  - (a) Vacuum
  - (b) 2 millitorr O_2
  - (c) 11 minute scan
  - (d) 30 minute scan
- Oxidation at 420°C
  - Rate Minimum
  - PuO (PuOC) is primary
- [Terada – 1969]



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

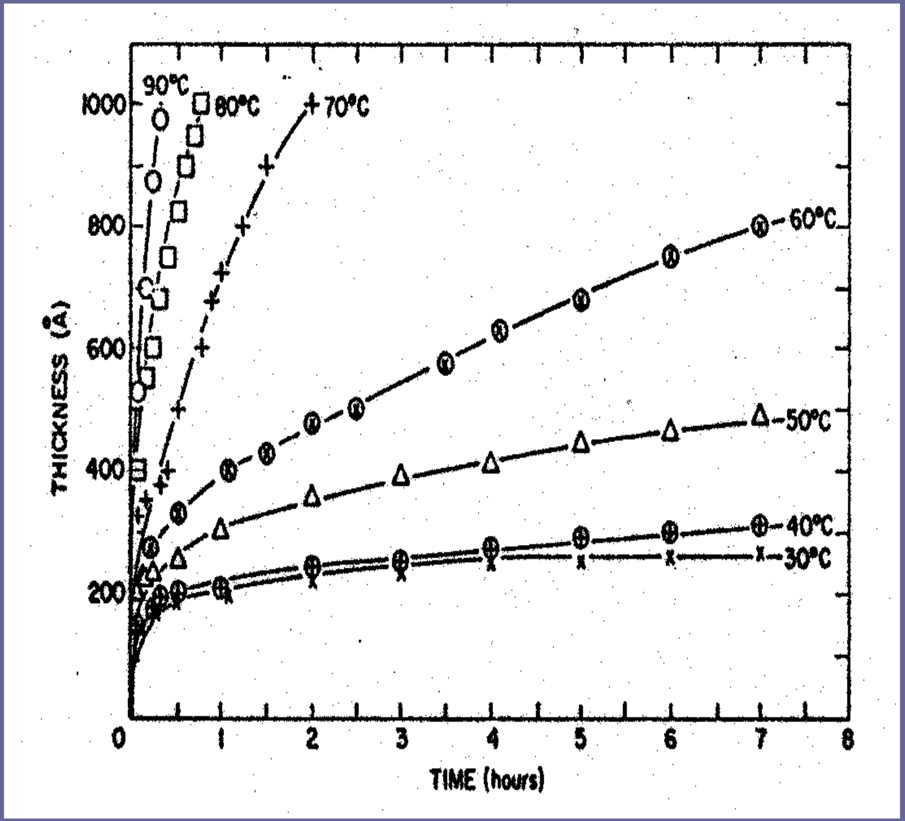
THE PROLIFIC YEARS 1960-1985

- Ellipsometer Measurements
  - Clean Pu coupons
  - Temperatures < 100°C
  - Oxygen atmosphere
  - Limiting oxide film thickness is ~1500Å
- Results
  - Limiting oxide film thickness is ~1500Å
  - Parabolic kinetics for films > 200-400Å and temperatures between 28 and 90°C
  - Retardation of oxidation by initial film of PuO (PuOC)
  - Product PuO_2

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Ellipsometric Measurement of Alloyed Pu Oxidation

- Alloyed Pu Oxidation
- Polished clean sample
- 5.0 x 10^{-2} Torr oxygen
- 30 to 90°C
- Measured oxide film thickness



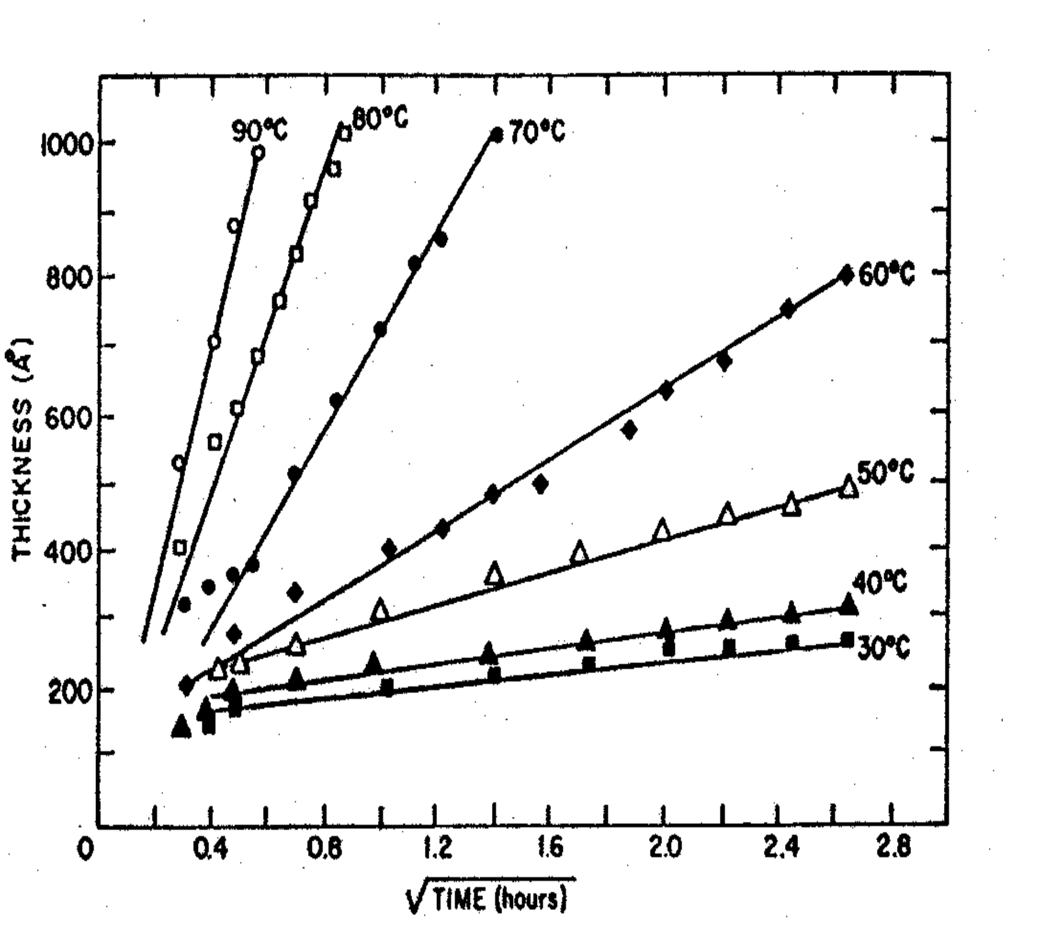
- Larson & Cash 1969

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Ellipsometric Measurement of Alloyed Pu Oxidation

- Alloyed Pu Oxidation
- Parabolic Rate for films greater than 200-400 Å
- Linear initial rate

- Larson & Cash 1969



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Oxide Film Thickness
Film Thickness vs. Color

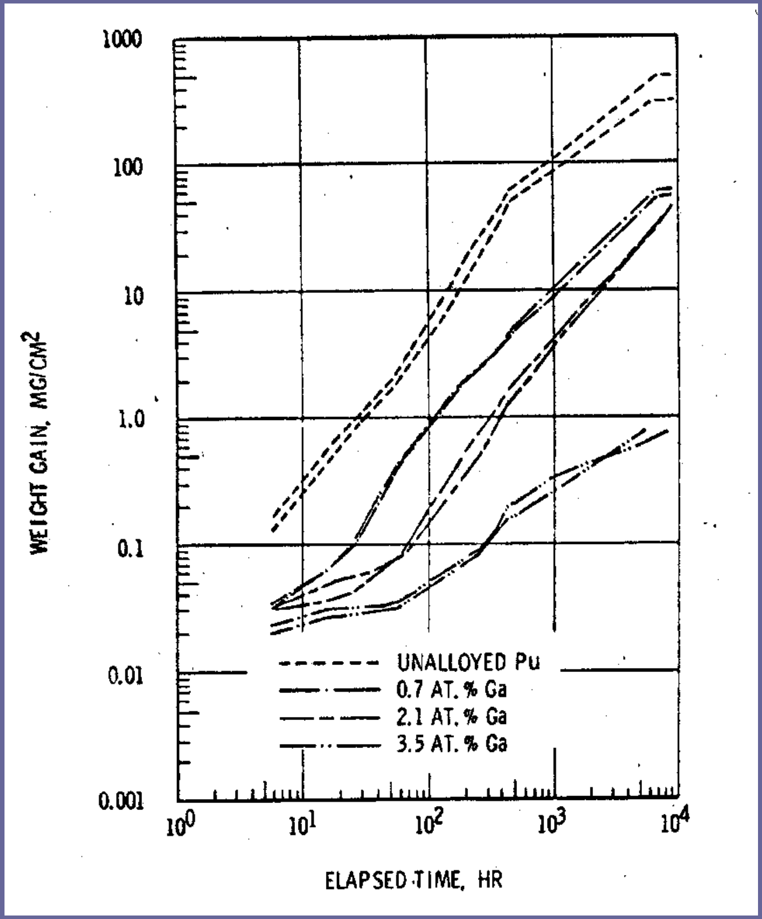
- Polished Pu coupon
- Argon Bombarded
- Exposed to 50μ O_2
- Temperature 30-90°C
- Ellipsometer Measure
- Visual Monitoring of 1st Order Colors

Neutral Silver	100Å
Gold	400Å
Red Violet	525Å
Violet	575Å
Purple	600Å
Blue	800Å
Silver Blue	1000Å

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

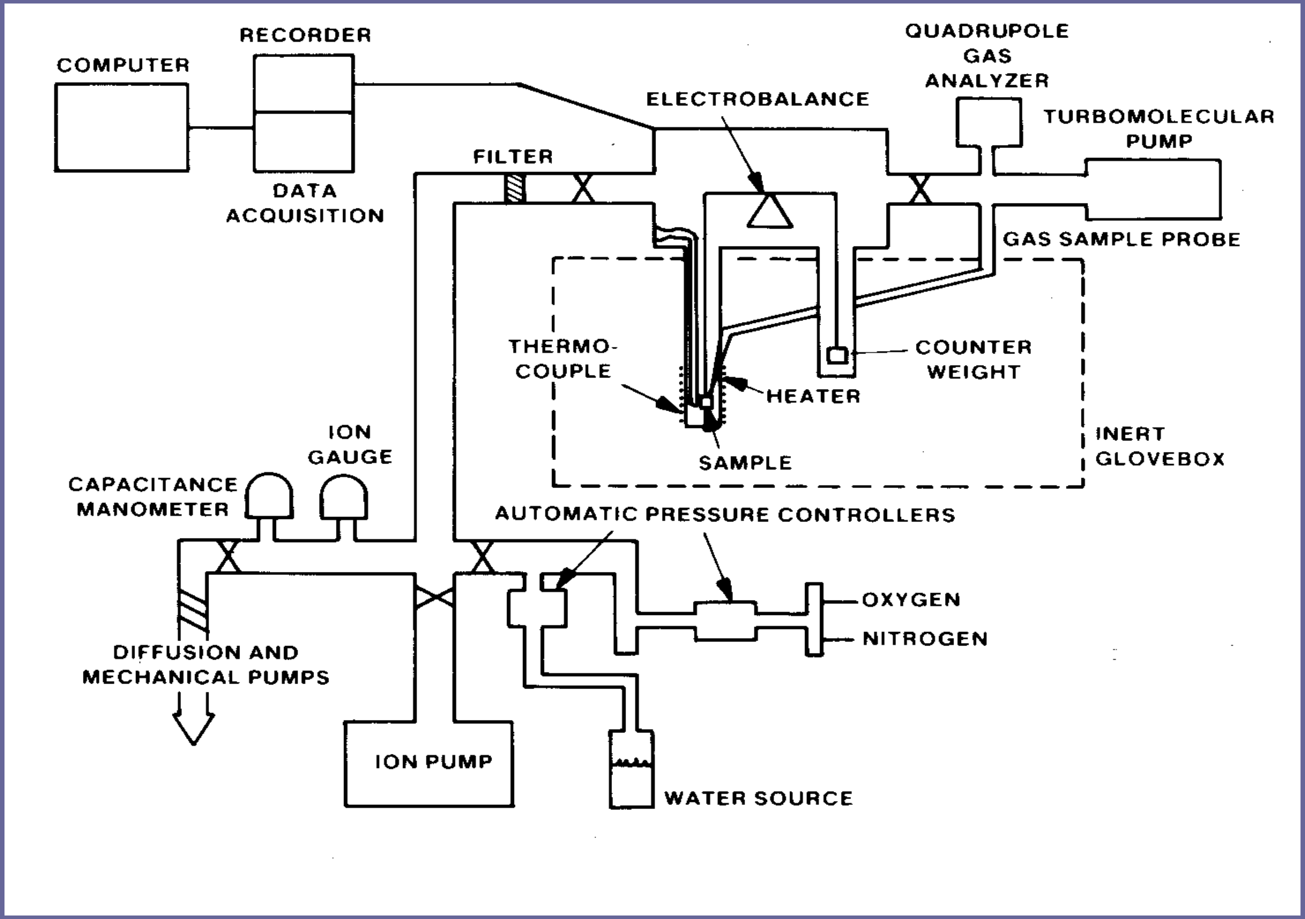
THE PROLIFIC YEARS 1960-1985

- Effect of Ga alloying
  - Air oxidation in moist air
  - Temperature 75°C
  - Rate decreases with Ga concentration
  - J. T. Waber - 1961
- Other alloys also decrease oxidation
  - Al (comparable to Ga), Zr, Ce, Zn, are less effective
- Some alloys enhance oxidation [ternary alloys]



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

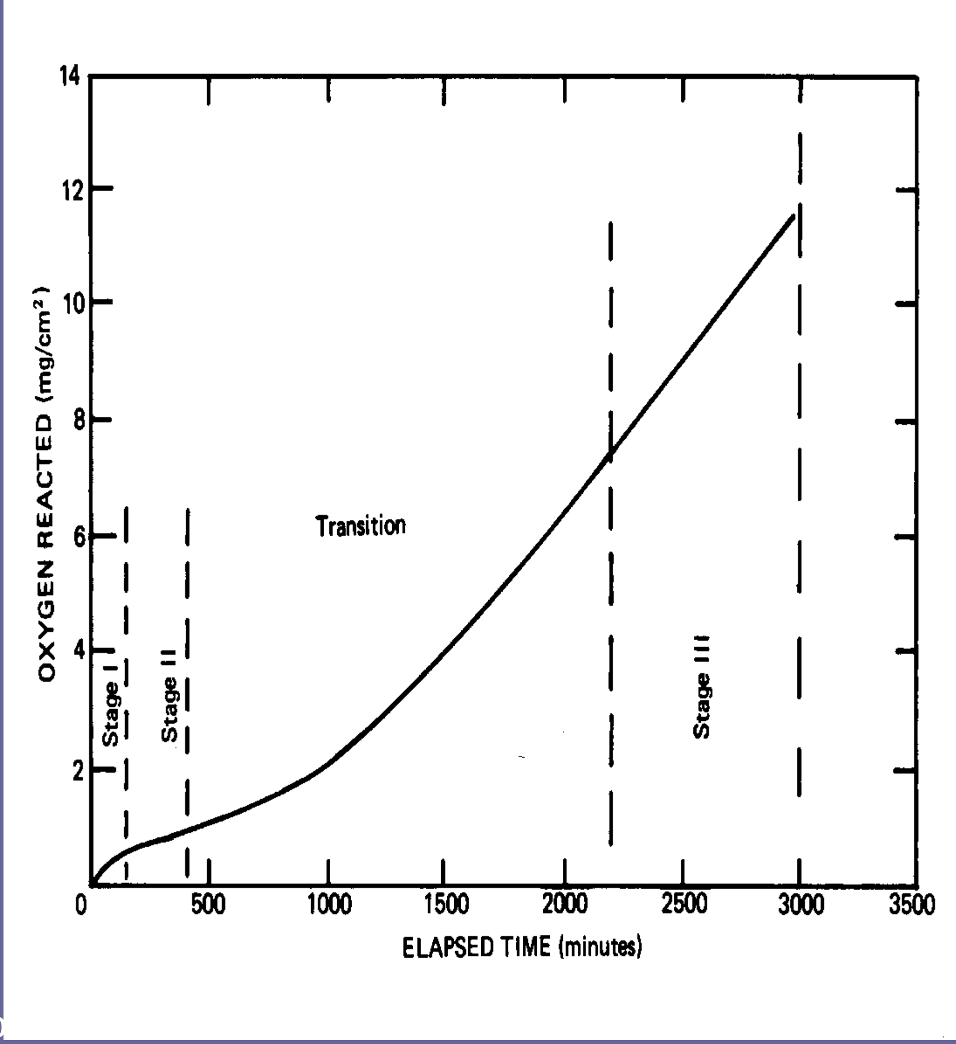
THE PROLIFIC YEARS
1960-1985
Experimental Apparatus



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

GALLIUM ALLOY OXIDATION - RFP

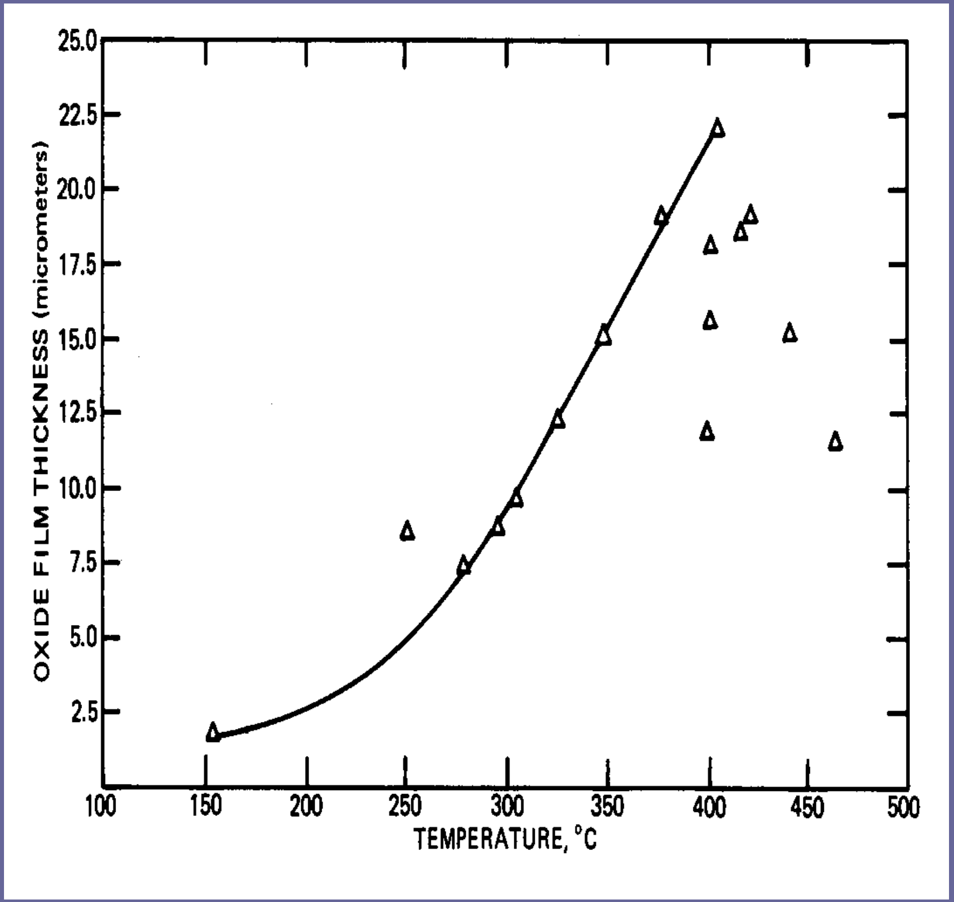
- Pu-Ga Alloy Oxidation
  - 150 - 500°C
  - Run at 278°C illustrated
  - 500 Torr dry air
- 3-Stage Oxidation
  - I Parabolic kinetics - diffusion controlled
  - II Linear kinetics - constant film thickness
  - III Linear kinetics - interface controlled
  - I + II Paralinear



Mr. J. L. Stakeb
contributer to the technical content
of this presentation. Mr. Allen is

GALLIUM ALLOY OXIDATION - RFP

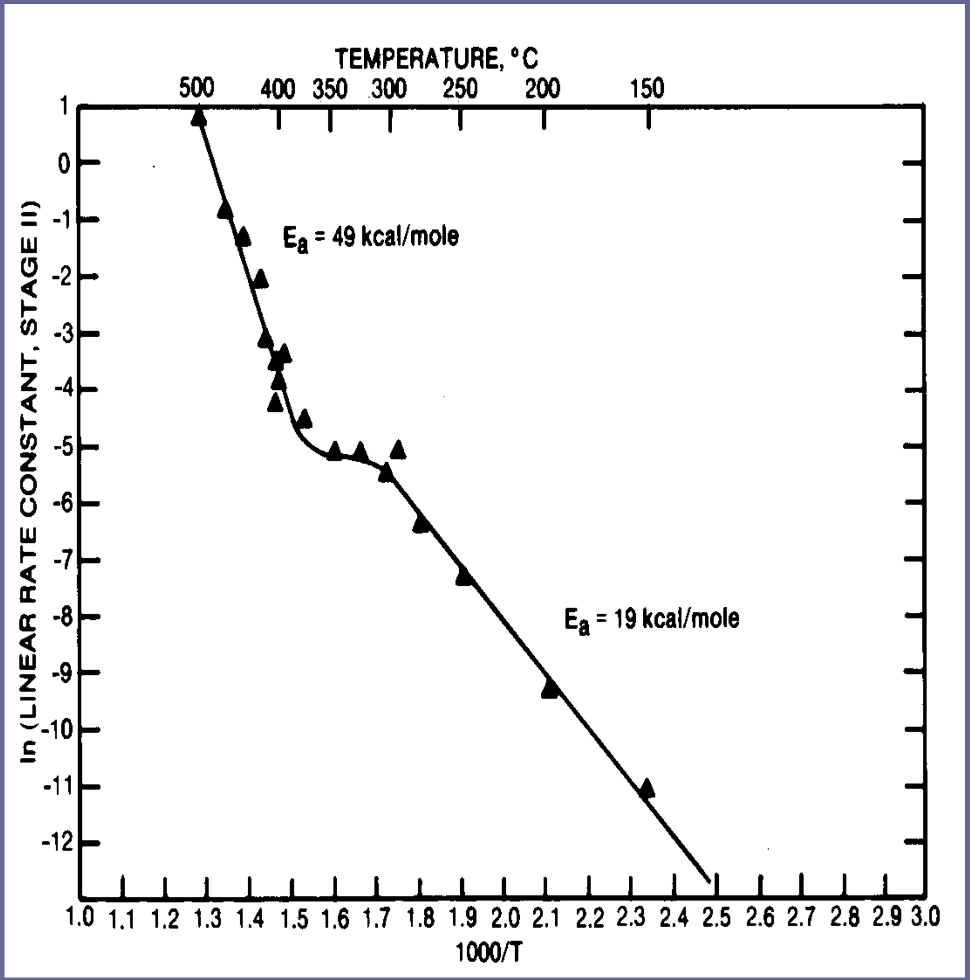
- Dense Oxide Film
  - Initial formation in parabolic stage
  - Thickness depends on temperature
  - Range 2 -22 micron
  - > 400°C thickness is unpredictable



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

GALLIUM ALLOY OXIDATION - RFP

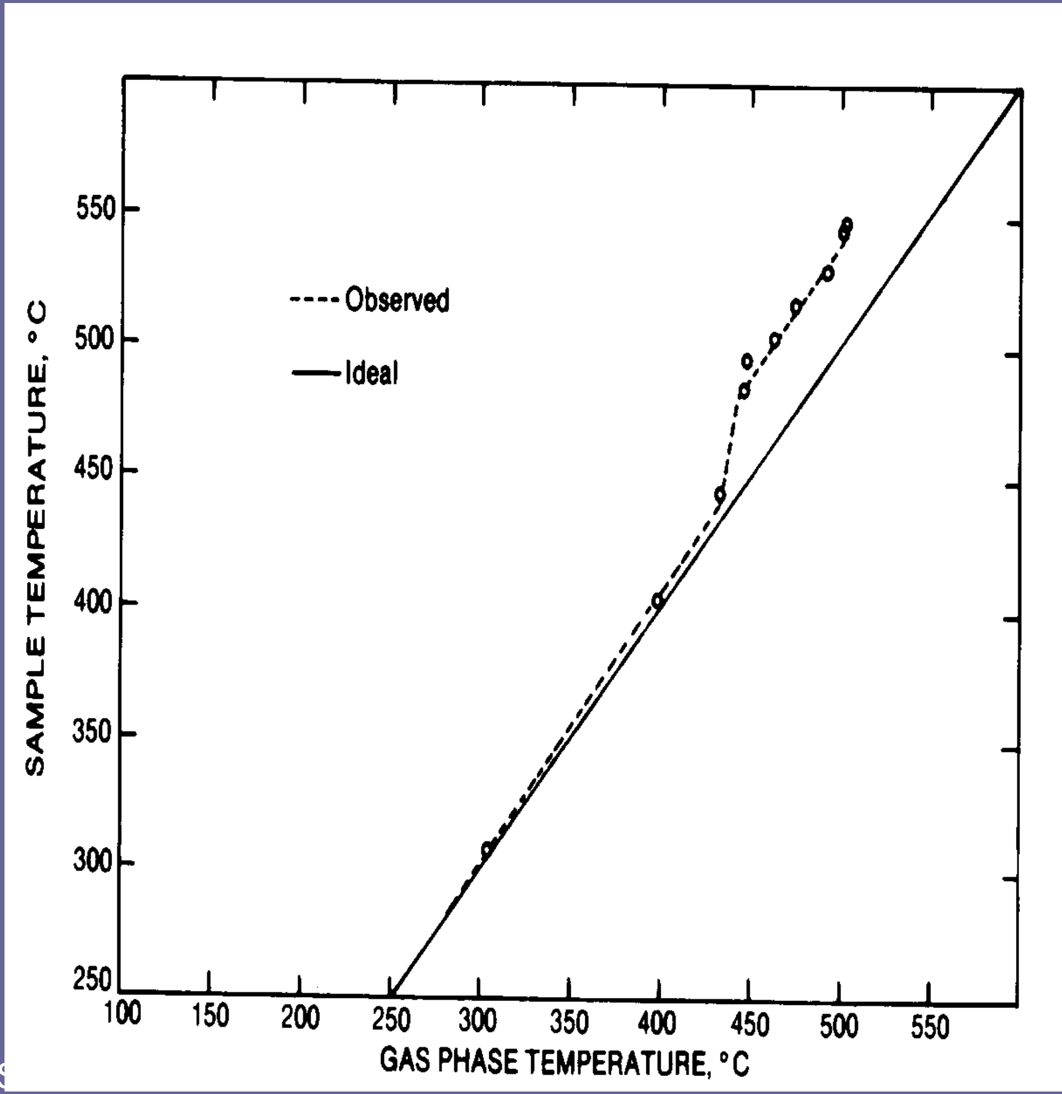
- Kinetic Temperature Dependence
  - Linear Stage II
  - Discontinuity between ~300-400°C
  - Suggests change in oxidation process or type of dense oxide



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

GALLIUM ALLOY OXIDATION - RFP

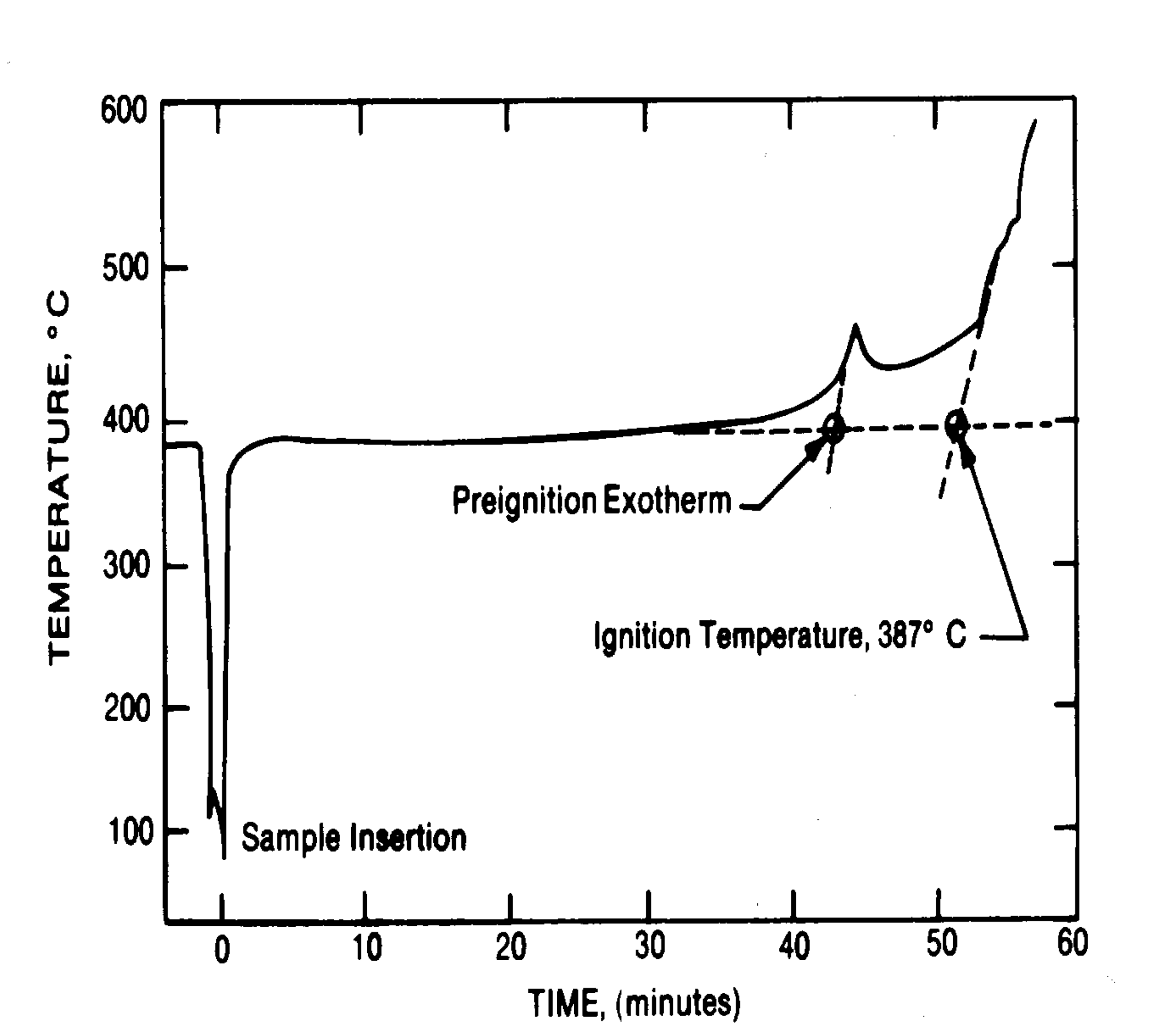
- Sample vs. Gas-Phase Temp.
  - Actual sample & gas T measured
  - Ideal (normal)
  - Observed sample
  - Exothermic heating > 435°C
  - Suggest onset of ignition



Mr. J. L. S
contributer to the technical content
of this presentation. Mr. Allen is

GALLIUM ALLOY OXIDATION - RFP

- Constant Temp. Ignition
  - Temperature differential shown previously likely the result of pre-ignition (Pitts '68)
  - Preignition here is for unalloyed Pu
  - Actual ignition was not observed
  - Ignition ~387°C



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

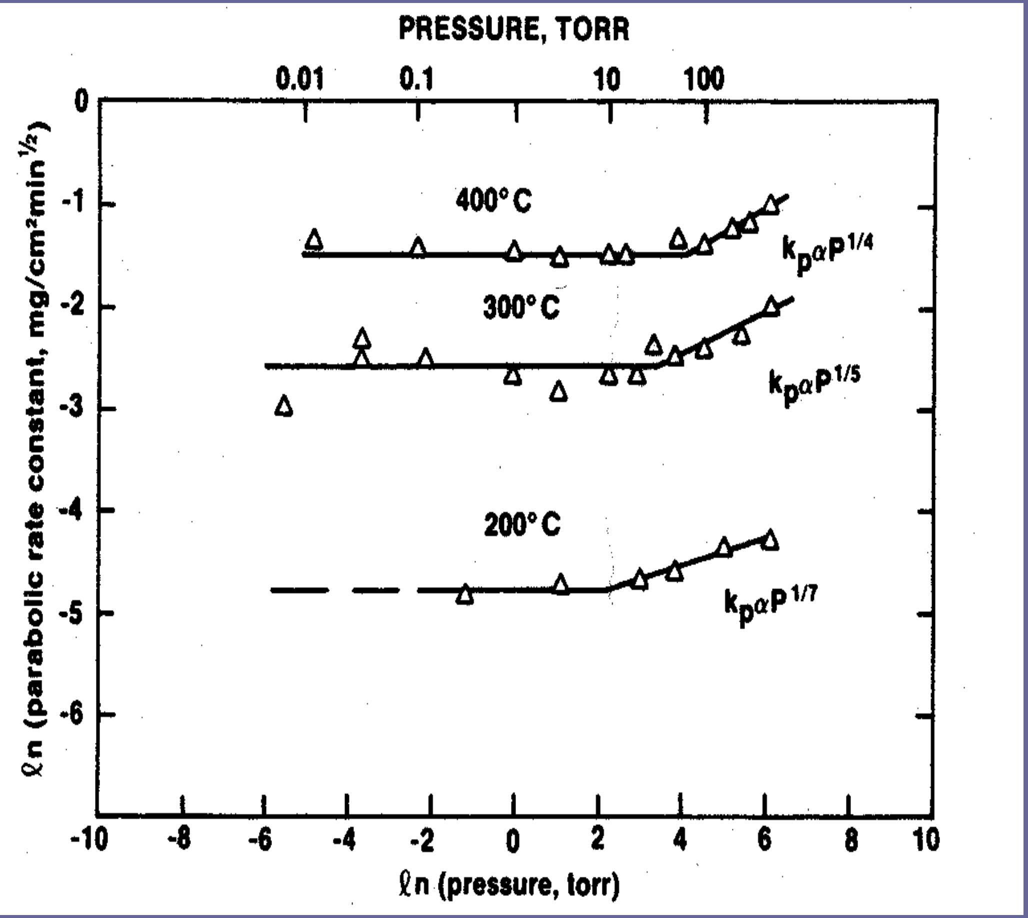
OXYGEN PRESSURE DEPENDENCE

- Alloy Oxidation in Oxygen at 150-500°C
- Oxygen Pressure 0.004 – 500 Torr
- Stage I & II Independent of pressure for P<60 Torr [Temperature dependent]
- P>60 Torr
  - k α $P^{1/7-1/2}$ [Temperature dependent]
- Stage III linear rate
  - Independent of pressure for P<37 Torr
  - k α P^{1} above 55 Torr and 400°C

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Oxygen Pressure Dependence

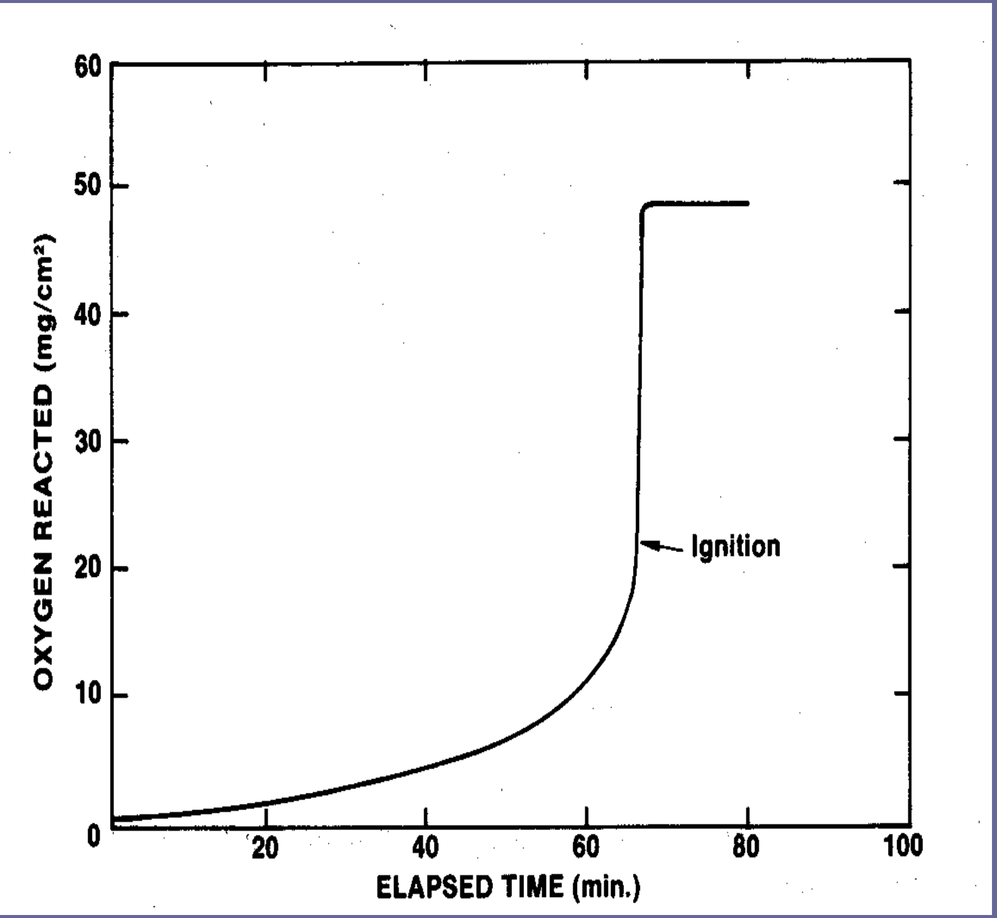
- Oxidation of Alloyed Pu – Stage I
  - Pressure independent at low P
  - Independent region is T dependent
  - Pressure dependent for P > 13 Torr



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

OXYGEN PRESSURE DEPENDENCE

- High Temperatures
  - 465°C and 10 Torr
  - Stage III depends on availability of O_2
  - O_2 chemisorption
  - Sticking probability controls

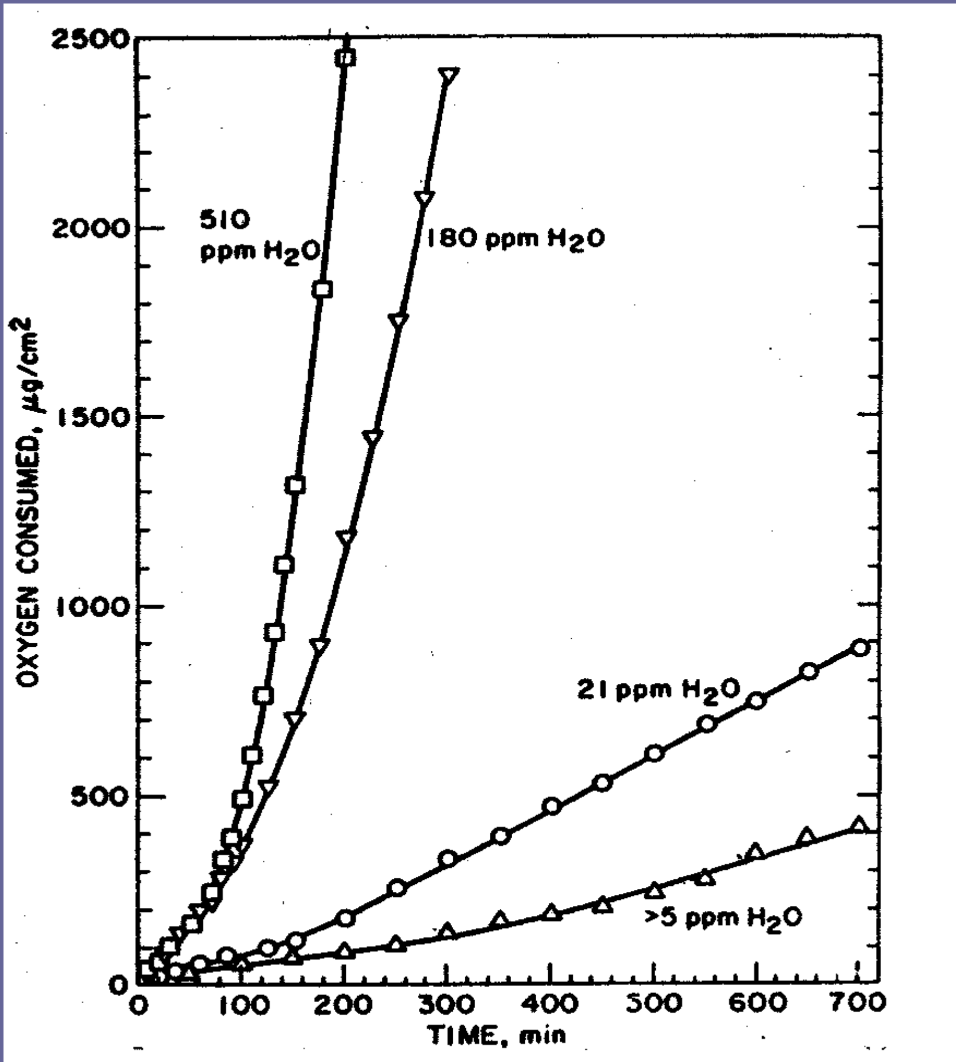


Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Effects of H_2O on Pu Oxidation

- Unalloyed Pu
- 190°C in oxygen
- Water accelerates oxidation
- No moisture effect above 215°C
- Effect greater in inert gases

- [Schnizlein and Fischer]



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

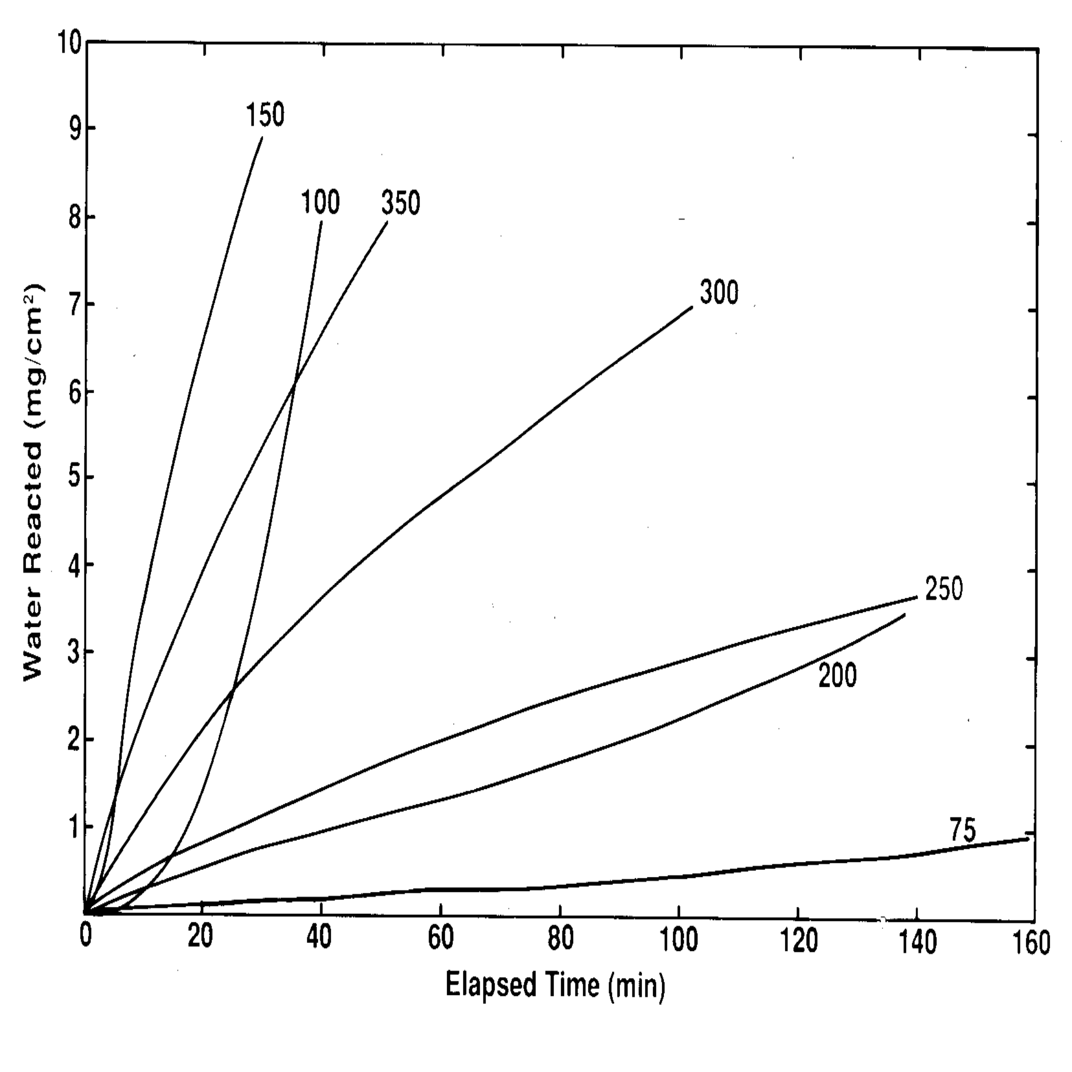
Effects of H_2O on Pu Oxidation

Glovebox oxidation of unalloyed Pu in air and nitrogen atmospheres

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

Plutonium-Water Reaction

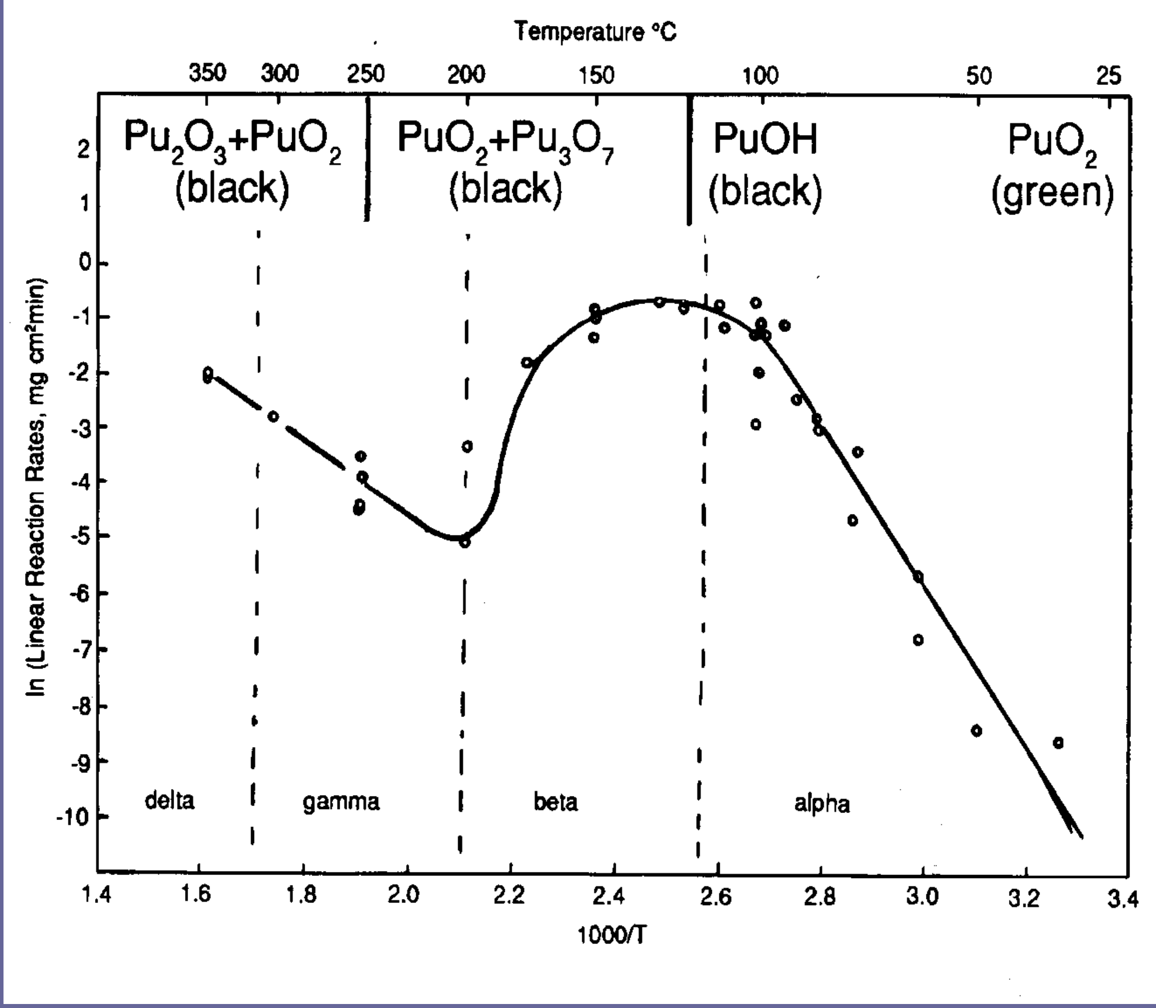
- Unalloyed Pu in 15 Torr H_2O Vapor
- Complex Temp. Behavior
- Multiple Products
- Changing Kinetics



Mr. J. L.
contributer
of this presentation. Mr. Allen is

Plutonium-Water Reaction

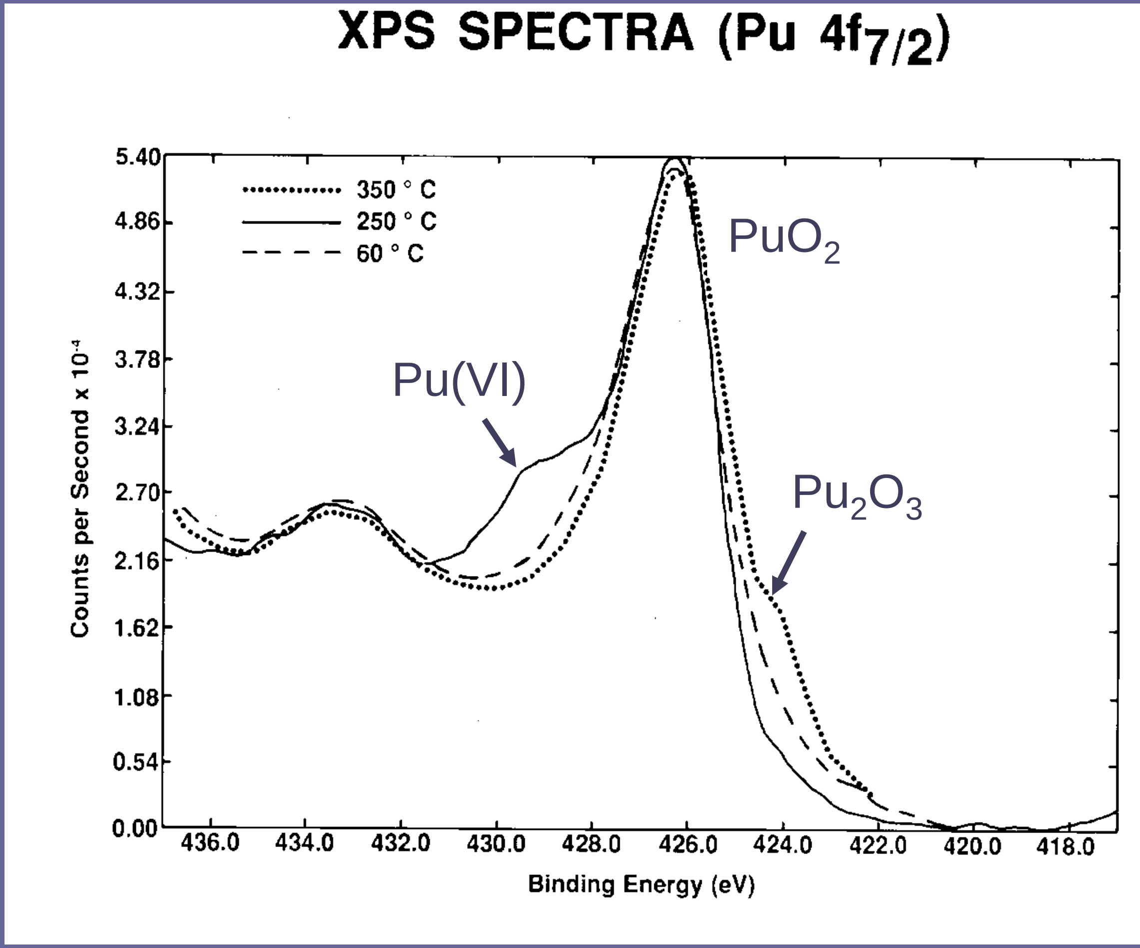
- Unalloyed Pu in 15 Torr H_2O
- Arrhenius Plot
  - Poor correlation with metal phase
  - Good correlation with products



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Plutonium-Water Reaction

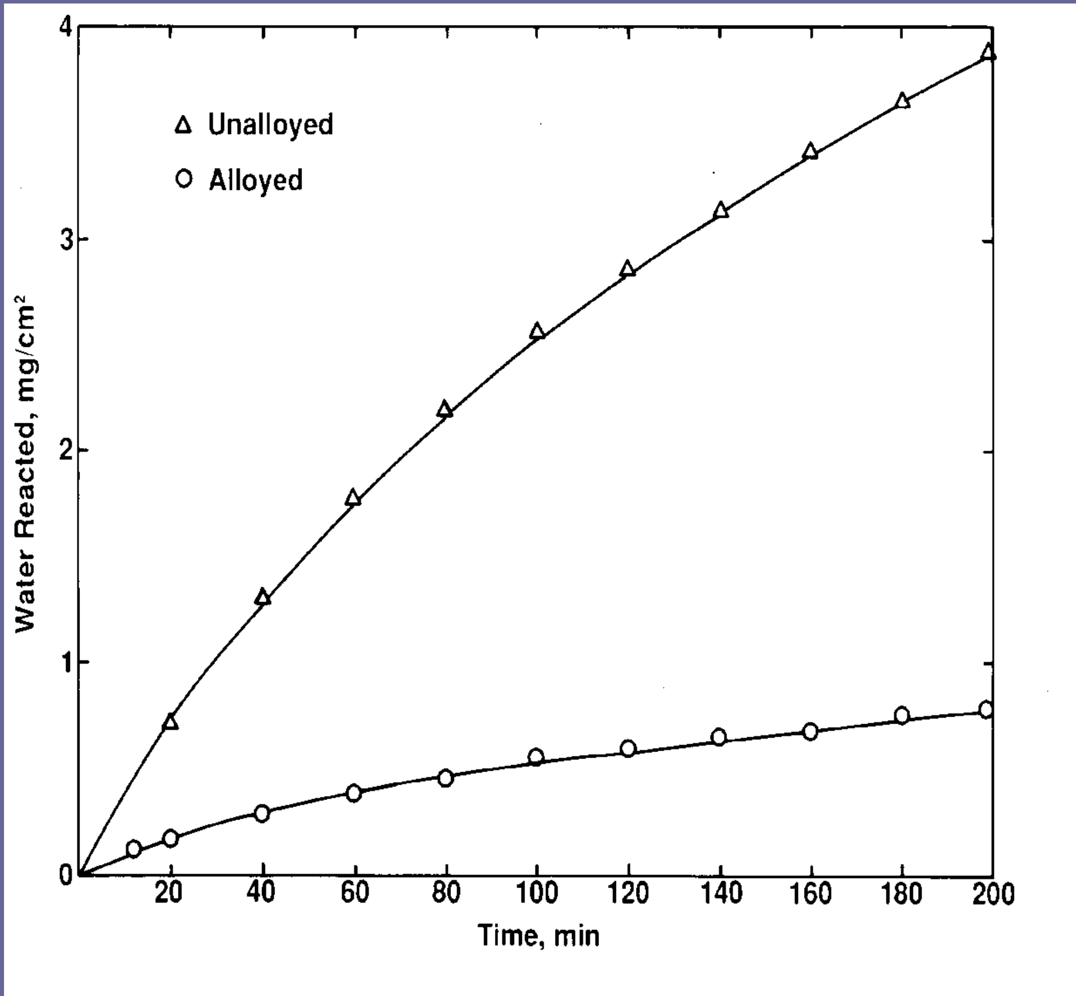
- Unalloyed Pu + Water Vapor
- PuO_2 at 60°C
- $PuO_2 + Pu_2O_3$ at 350°C
- New Oxide Peak at 250°C
- BE Correlates to Pu(VI)



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Plutonium-Water Reaction

- Data for 250°C & 15 Torr water
- Unalloyed rate ~5 X alloyed rate
- Diverse Products
  - PuH_2
  - PuOH
  - Pu_2O_3
  - PuO_2
  - $PuO_{2+\delta}$



Mr. J. L.
contributer to the technical content
of this presentation. Mr. Allen is

Plutonium-Water Reaction

- Unalloyed Pu reaction with water vapor
- 250°C, 15 Torr water
- Localized pitting
- The presence of a uniform hydride layer at the metal interface is unknown

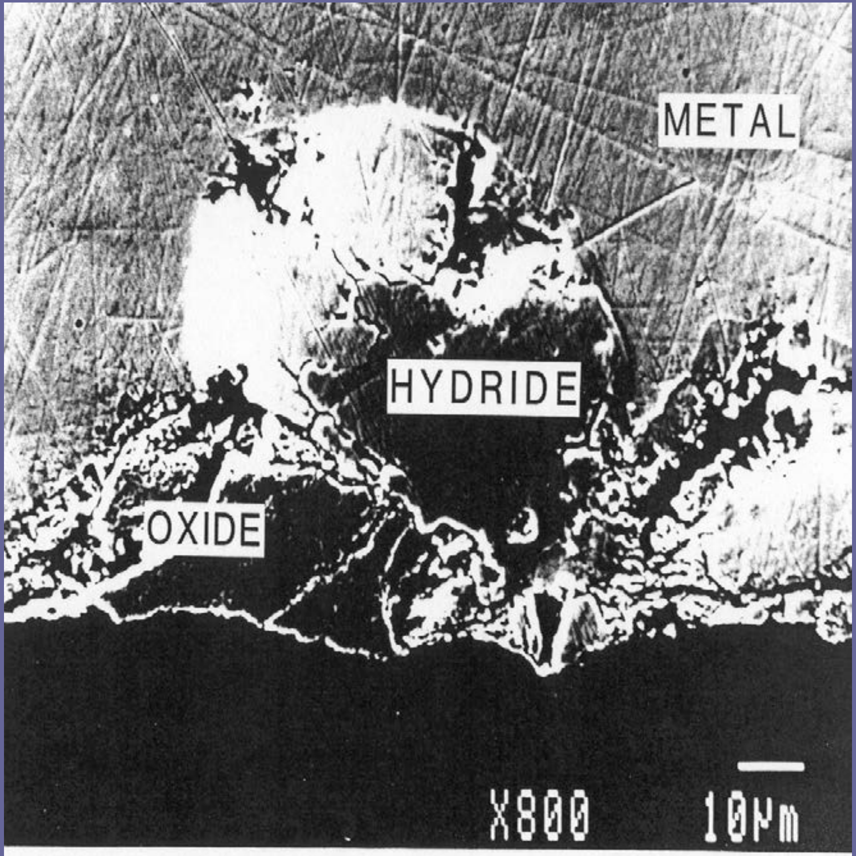
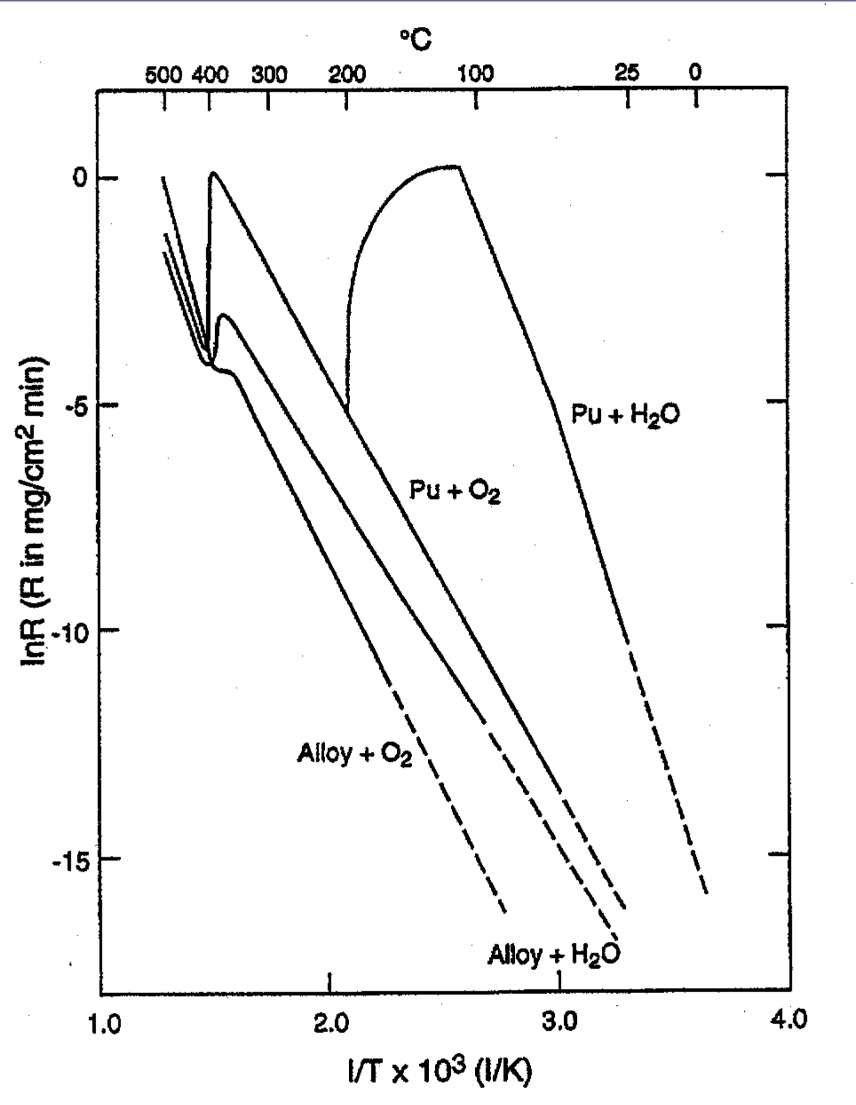


Figure 7. Photomicrograph of the product layer formed by the reaction of water vapor with unalloyed plutonium at 250 °C. Magnification is 800×.

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Summary: Pu Oxidation
Alloy, Oxygen, Moisture Effects

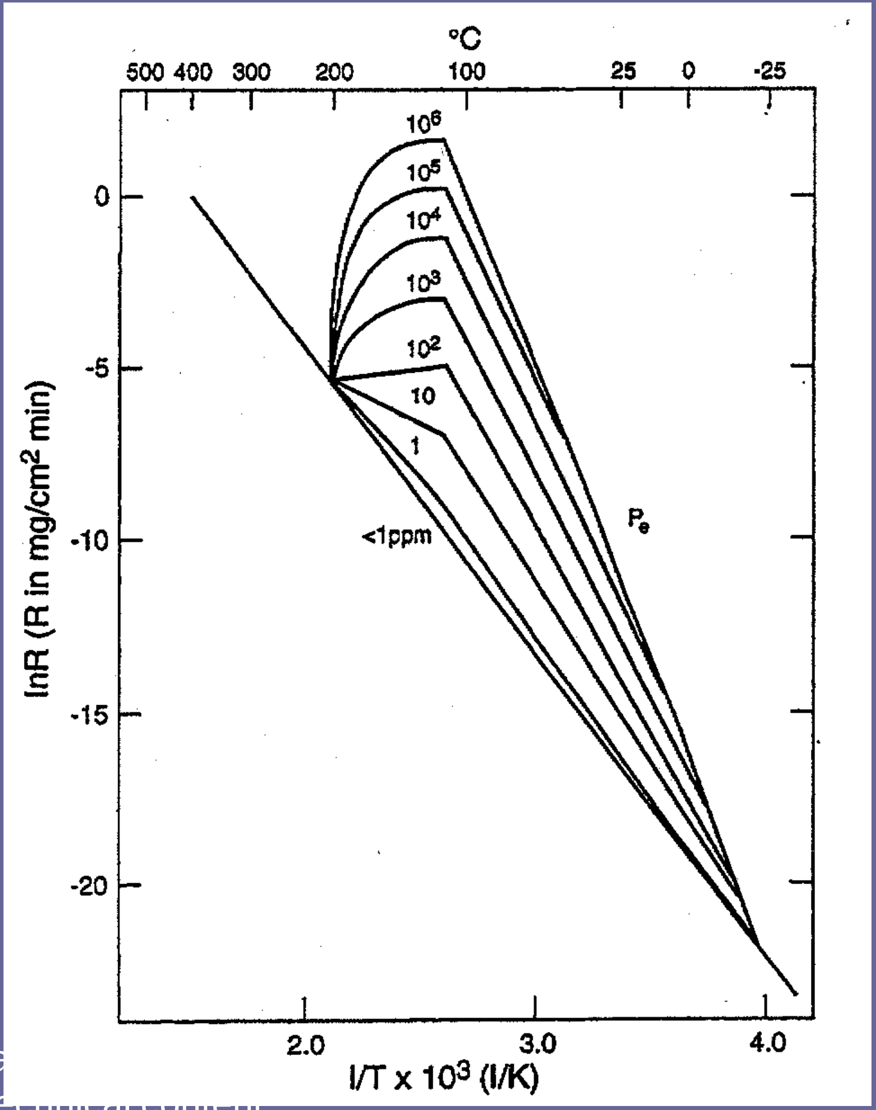
- Kinetics in H_2O and O_2 are:
  - H_2O dependent < 200°C
  - H_2O independent > 200°C
  - O_2 independent < 200 °C
- Alloying
  - Rate Suppressing
  - Suppression exceeds enhancement by H_2O
  - Effect only < 400°C



Mr. J. L. Stakebake is contributer to the technical content of this presentation. Mr. Allen is

Summary: Pu Oxidation
Moisture Effects on Pu Oxidation in Air

- Rate (R) α $[H_2O]^n$
  - n is temperature dependent
- Effects of H_2O persistent < 200°C as long as O_2 is present
- R (25°C,25 Torr H_2) is 200 times faster than R (25°C, 160 Torr O_2)



Mr. J. L. Stakeba[...] contributer to the technical content of this presentation. Mr. Allen is

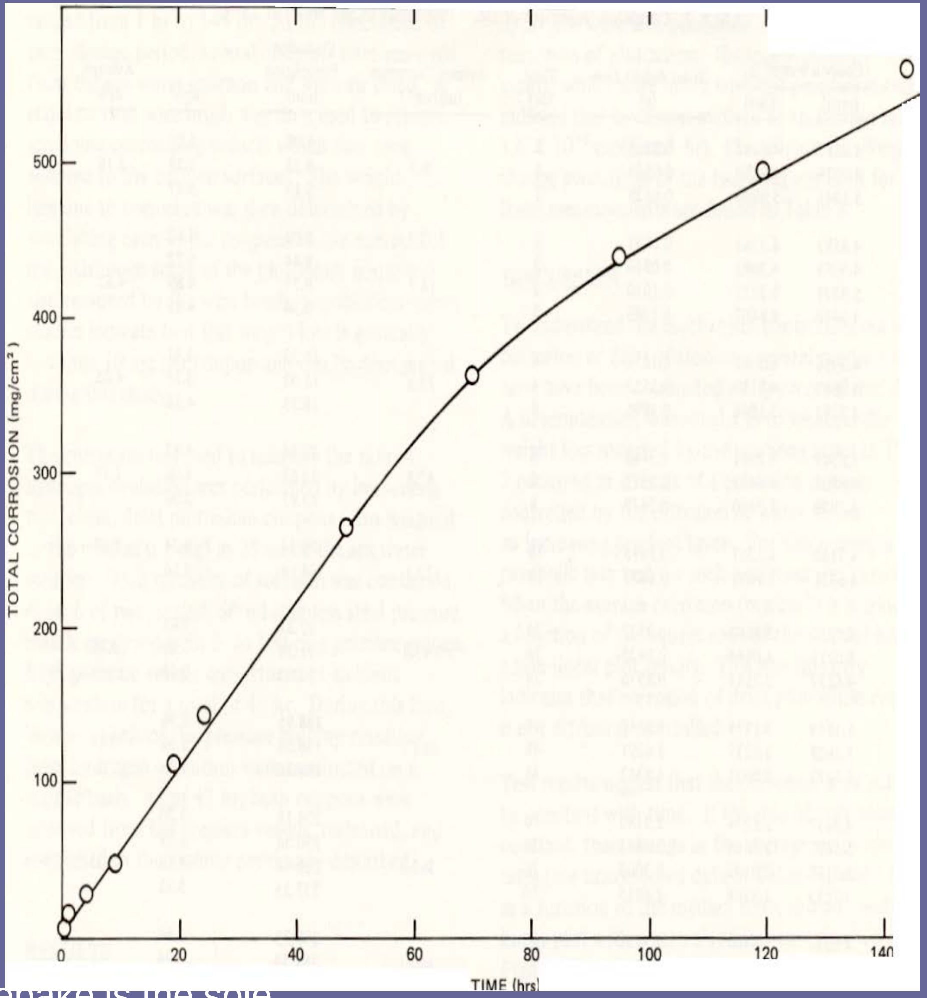
Summary Oxidation Kinetics

- General:
  - $R = k\exp(-E_a/R^*T)(PO_2)^m(PH_2O)^n$
    - [kinetic description depends on determining m, n, and E_a]
- Moisture Independent Region (T > 200°C)
  - lnR(R in mg cm^{-2} min^{-1}) = 13.68 – (9010)/T
- Moisture Dependent Region (T < 200°C)
  - $\ln R = -12.60 + 0.498 \ln P_{H2O}$

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Corrosion of Pu in Sea Water

- Closed αPu System
- Vented with sea water
- Change of geometry by corrosion products?
  - Oxides
  - Hydrogen
- Kinetics of reactions
  - k $(mg/cm^2) = 6.43t - 0.01706t^2$

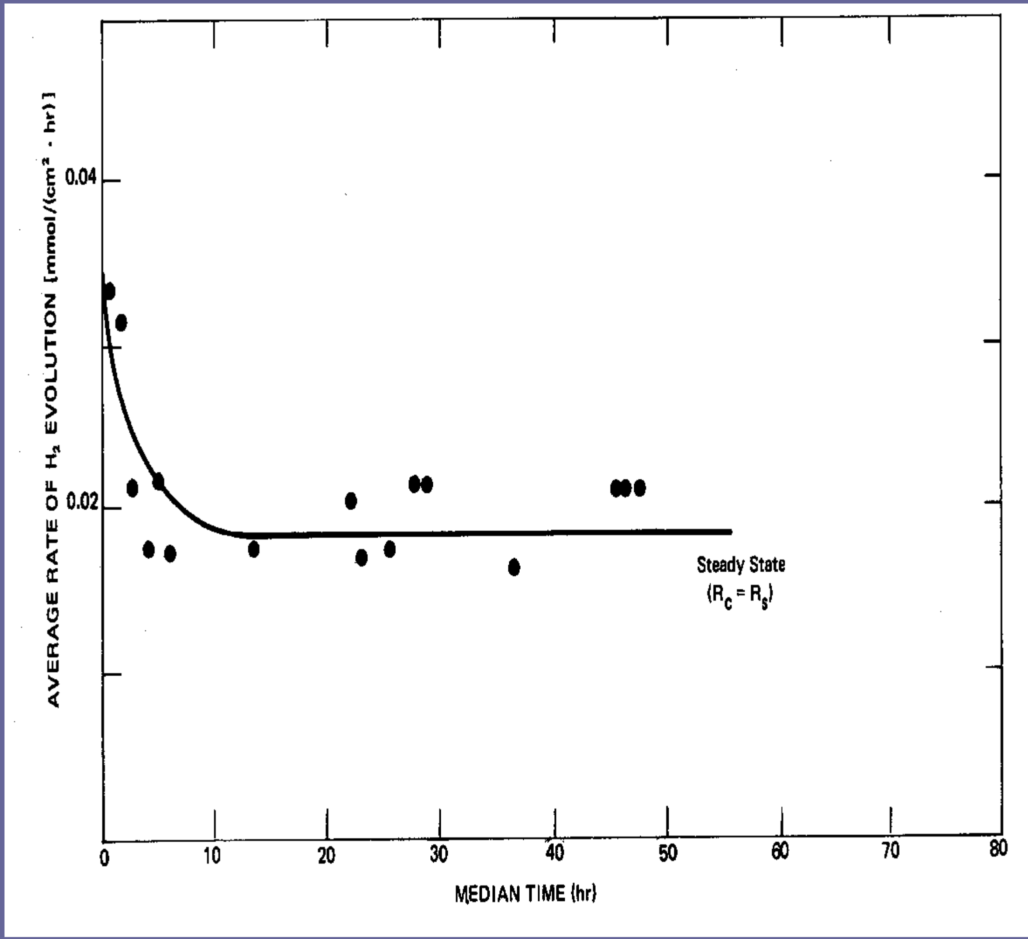


Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Corrosion of α Pu in Sea Water

- Products
- Solid
  - $Pu(OH)_4 \cdot X\ H_2O$
- Gas
  - H_2
  - 1.6×10^{-5} (mol/cm^{2}hr)

- Hodges, Haschke, Reynolds - 1979



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Plutonium Pyrophoricity

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Plutonium Pyrophoricity

- Metal Burning
  - Chemical Oxidation
  - Surface Reaction
  - Exothermic
  - Reaction Controlled Kinetics

- Combustible Burning
  - Chemical Breakdown
  - Vapor Phase Reaction
  - Exothermic
  - Gas Diffusion Controlled

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

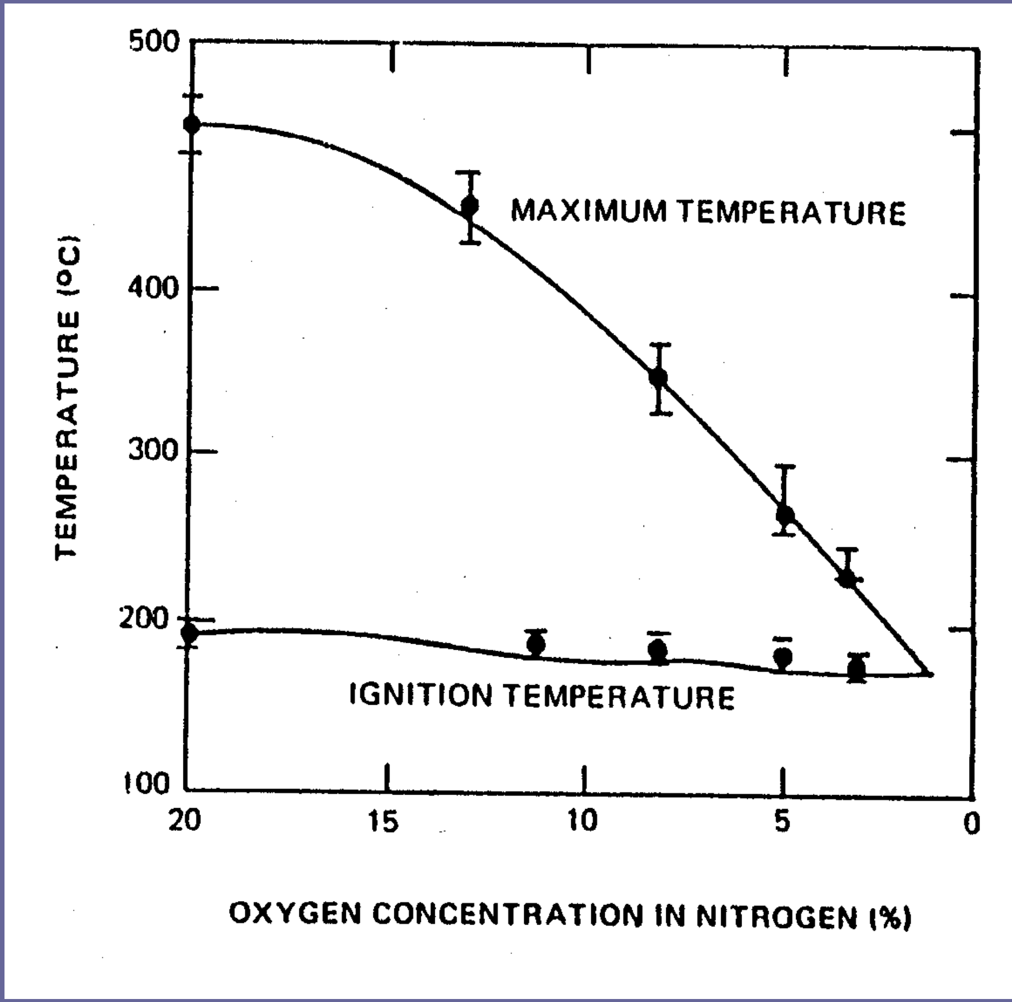
Plutonium Pyrophoricity

- Ignition of 2kg Pu ingot
- Stored in produce can
- Exposed to water vapor
- Corrosion ruptured the can

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

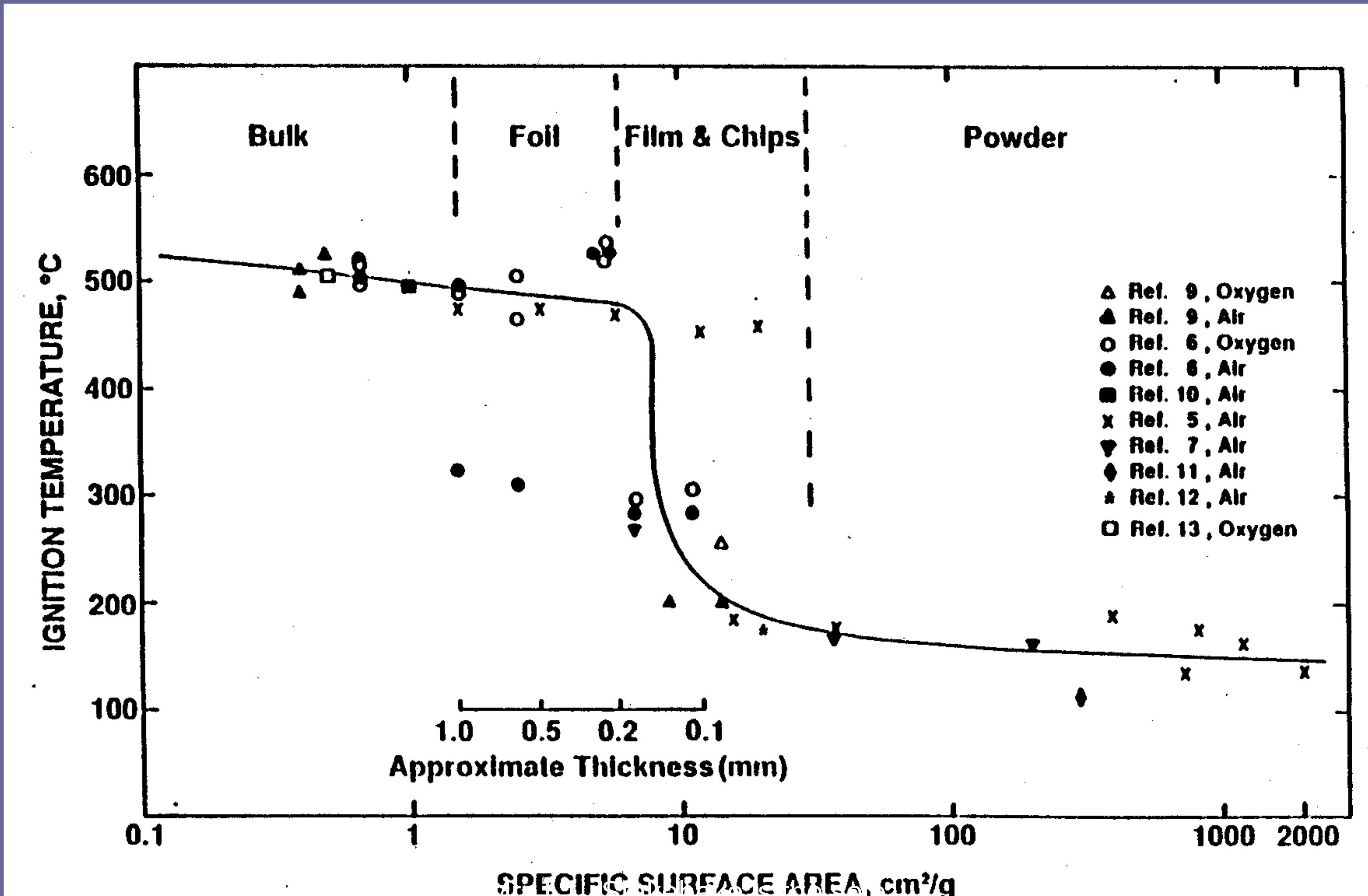
Plutonium Ignition Studies

- Effects of Oxygen
  - Alloyed Pu
  - 140 mesh filings
  - Oxygen concentration
    - 3-22%
- Findings
  - No ignition in < 3% O_2
  - Ignition temperature constant
  - Burning temperature decreases with O_2



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Geometrical Effects on Pu Ignition



contributer to the technical content
of this presentation. Mr. Allen is

Examples of Pyrophoric Pu

- Pyrophoric Residues
  - Unburned Brushed Oxide, Floor Sweepings, Casting Slag
- Pyrophoric Metal / Compounds
  - Plutonium Hydride
  - Plutonium Chips, Turnings, Films
- Specifically
  - Pu metal < 0.5 mm thick or weighing < 2 g

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Mechanism for Pu Pyrophoricity

- Ignition Temperature
  - Surface: Mass Ratio
  - Particle Size
- Critical Dimensions
  - 0.25 mm diameter
  - 0.088 mm thickness
- Ignition Temperature
  - > 475-525°C

- Sample Heating
  - $Pu_2O_3 \rightarrow PuO_2$
  - Adiabatic heating of particles of less than critical dimensions
  - External heating of larger particles
- Good Agreement with observations

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Metal Explosibility

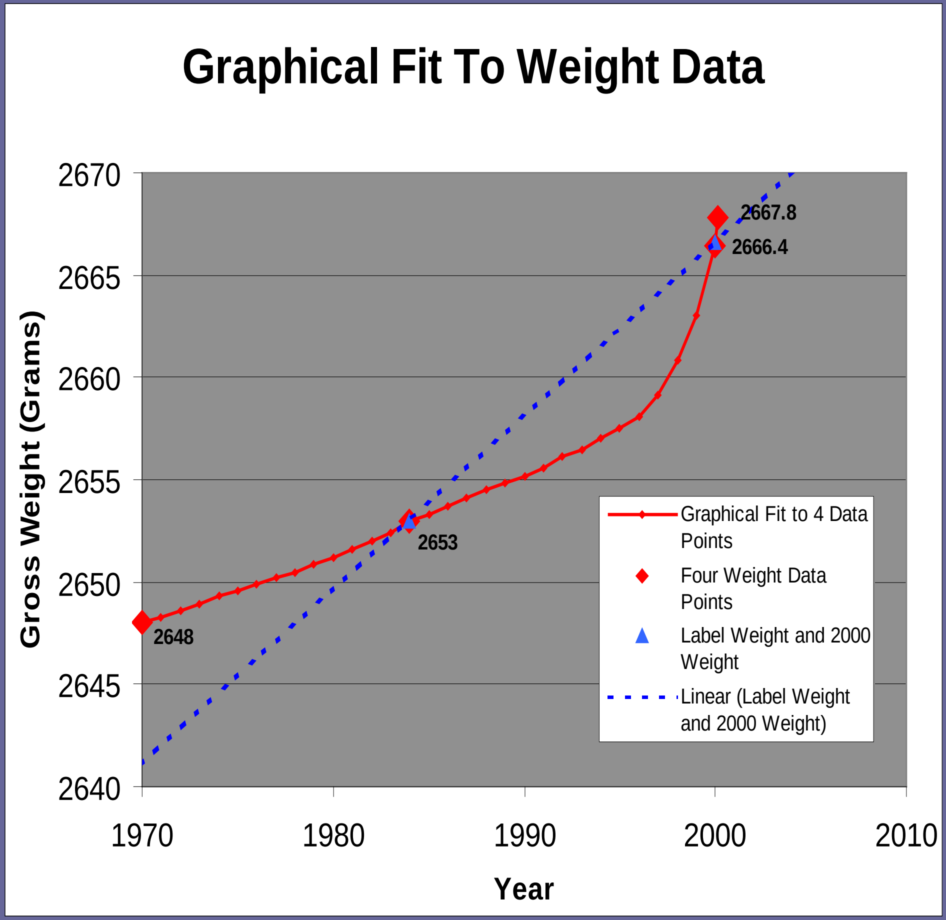
- **<u>Uranium Ignition</u>**
- Conditions
  - < 10 micron particles
  - Dispersed cloud
- Temperature, 20°C
- Pressures
  - 40-50 psig, max
  - 3000-7000 psi/sec

- **<u>Plutonium Ignition</u>**
- Conditions
  - <1 mm particles
  - Individual laser ignition
  - 40% exploded
- Energy
  - Not measured
  - Appeared less then U

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

Pu Storage Issues
Container Failures

- Causes
  - Metal Oxidation
    - Can seal leak
    - Pu oxidation
    - Volume expansion fails can
  - Gas Pressurization
    - Moisture
    - Organics



Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Failed Container
RF Produce Can

- ~ 2 kg Pu Ingot
- Repeated exposure to water bath
- Failure occurred when corrosion products expanded

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

Requirements for Safe Storage
DOE Standard 3013

- Calcination of oxide
  - – Removal of organics
  - – Removal of water
- Good Container
  - – Pressure resistant
  - – Corrosion resistant
  - – Proper sealing

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Consequences of Not Meeting the Criteria

- Inner 3013 can
- Weld defect not detected
- Metal button stored in SRS vault
- Oxidation produced oxide that was released during storage and transfer

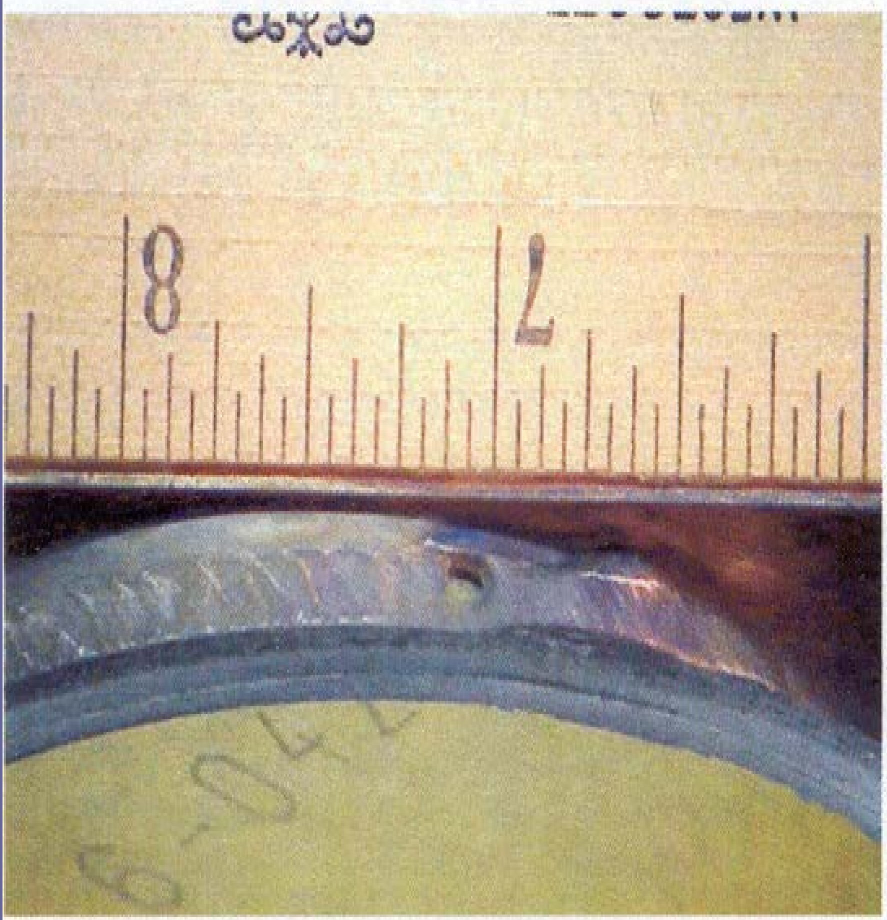


Figure 2-3 Weld Defect

Mr. J. L. Stakebak... contributer to the te... of this presentatio...

Potential Problems with Metal Stabilization

- Pure Pu Button (Hanford)
- Burned in air in a Hasteloy tray
- Product presumed to be an oxidation resistant Pu-Ni alloy

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Potential Problems with Oxide Stabilization

- Oxide feed material produced by Pu metal oxidation
- Pre-burning did not convert all Pu to oxide
- Molten Pu corrosion of Inconel tray coated with Al

Mr. J. L. Stakebake is the sole contributer to the technical content of this presentation. Mr. Allen is

Conclusions

- Objectives for early studies
  - Desire for rapid accumulation of data
    - Pu availability was limited
    - Use of bounding conditions
      - High Temperature
      - High Humidity
    - Application need was immediate
  - Choice of instrumentation was limited
    - Some measurements made under unrealistic conditions; e.g. ellipsometry

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

Conclusions

- Objectives for studies in the prolific years
  - Need for defining behavior in production environments
    - New Pu alloys
    - New methods of production
    - Better environmental controls in gloveboxes
  - Need for capability to predict oxidation behavior
  - Availability of better instrumentation

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

Conclusions

- Where are the holes in our knowledge?
  - Data needed under real conditions
    - Temperatures of 0 to 200°C
    - Moisture levels 200 to 20,000 ppm
  - Moisture dependent region needs data
  - Better instrumentation needs to be used
    - Kinetic measurements
    - Product characterization
  - Proposed models need further validation

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is

Acknowledgements

- Key Review Articles
  - O. J. Wick, "*Plutonium Handbook*" (1980)
  - Jerry L. Stakebake, "The Storage Behavior of Plutonium Metal, Alloys, and Oxide", J. Nucl. Mater. 38, (1971) 241
  - C. A. Colmenares, Prog. Solid State Chem., 9 (1975) 139
  - C. A. Colmenares, Prog. Solid State Chem., 15 (1984) 257
  - J. C. Martz, J. M. Haschke. J. L. Stakebake, "A Mechanism for Plutonium Pyrophoricity", J. Nucl. Mater. 210 (1994) 130
  - T. C. Totemeier, " Review of the Corrosion and Pyrophoricity Behavior of Uranium and Plutonium", West Report ANL/ED/95-2 (1995)
  - J. M. Haschke and J. L. Stakebake, "Handling, Storage, and Disposition of Plutonium and Uranium", *Chemistry of the Actinide and Transactinide Elements*" (2003) in press

Mr. J. L. Stakebake is the sole
contributer to the technical content
of this presentation. Mr. Allen is